Estimating the cost of extracting cereal protein with ethanol

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Abstract

Most cereals contain prolamine-rich proteins, which are water insoluble, but soluble in alcohol solutions. These proteins could be used as constituents of temporary, environmentally stable coatings and films. It may be economically feasible to separate these proteins as part of a starch to ethanol process, if the alcohol solvent separation and recovery cost are low enough. Estimates of separated protein product cost can be made using a separation process simulation developed for maize. A general cost model was formulated as the sum of two major energy-consuming units, distillation and product drying, and three other overall cost fractions based on two mass flow ratios, namely, the solvent to cereal feed and the product to feed. Model coefficients were calculated from fits of the simulation cost predictions for zein extraction. Published by Elsevier Science B.V.

Keywords: Cereal protein; Protein extraction; Zein

1. Introduction

In 1995, 1.5 billion bushels (38 million tonnes) of corn were converted to starch or starch derivatives such as dextrose, corn syrup and ethanol in wet and dry mills. This was accompanied by coproduction of over 3 million tonnes of corn protein-containing mixtures, which were sold as animal feed at approximately \$0.1/kg. A substan-

tial fraction of this was sold in Europe. The European corn and corn gluten market is unstable, partly due to controversy about genetic modification of US corn. If concentrated and purified, this protein may compete with isolates such as soy protein with an average price of \$0.50/kg. The vegetable protein market is growing. The Soy Protein Council (personal communication, 1999) projects a 1 million tonne (50% flour equivalent) market for US produced edible soy protein. Vegetable protein also has a substantial potential market as biodegradable films for farm mulch, erosion control, trash bags, diaper liners and cardboard coating. However, competition for the biodegradable polymer market exists from synthetic polymers as well as from extracts of other undervalued agricultural vegetable coprod-

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ucts such as soapstock, the residue from extractions of edible oils such as cottonseed, safflower and sunflower seed. About 30–50 thousand tonnes/year of cottonseed residue are sold as animal feed. The polymer, polylactic acid, can cost about the same as soy protein isolate, \$0.5/kg when produced in sufficient quantity, 50 thousand tonnes/year or more (Bohlmann, 1997). The size of the industrial markets for vegetable protein is sensitive to cost and biodegradability is not expected to compensate for properties or cost inferior to the polymers conventionally used.

Maize (Zea mays) protein content depends on plant variety and growing conditions. Dent maize hybrids are the most common variety selected for wet-milling. An analysis of 27 hybrids showed a protein content ranging from 7.9 to 9.6% with a mean of 8.7% (Fox et al., 1992). The prolaminerich protein fraction, called zein, is composed of high proportions of glutamic acid and proline, is soluble in 70–90% ethanol, but insoluble in water or salt solutions. Based on biological function, zeins are storage proteins because they are formed and accumulated in the later stages of the seed development and are used as substrate for the sprouting plant, in contrast to the metabolic proteins, which implement the sprouting and plant growth (Lasztity, 1996). Zein is distributed in the endosperm, in protein bodies in a thin glutelin matrix between starch granules.

An important extraction parameter is the fraction of the product material (protein) extracted, which is dependent on the process conditions that control recovery: temperature, time, particle size of milled maize, mechanical agitation, and solvent and chemical use. Protein recoveries of 2 and 5% for corn milled to 2 and 0.02 mm, respectively, can be obtained by extracting at 25°C, for 1 h, with mixing sufficient to suspend the 10-kg batches of maize in 70% ethanol at a ratio (w/w) of liquid to maize of 4:1 (Dickey et al., 1998). A more vigorous laboratory process can recover 57% protein where flaked maize was extracted with 45% ethanol-55% 0.1 M NaOH (v/v) in stages (Hojilla-Evangelista et al., 1992). This process began with a 15:1 ratio of liquid to maize and ground in a blender and held for 2 h. A nearly equal mass of ethanol-alkali liquid was added,

blended and heated to 55°C, followed by shaking at 130 rpm for 2 h. Patented, and published, maize extraction processes, (Russell and Tsao, 1982; Lawhon, 1986; Chen and Hoff, 1987) report recoveries intermediate to these bounding cases (2–57%).

2. Materials and methods

2.1. Experimental

Maize extractions were made to provide data used in creating the simulation process flow diagram (Fig. 1). The process was similar to the 19-29°C extractions described by Dickey et al. (1998), but at a higher temperature, 50°C. Dent maize, milled to a median size of 2 mm, was obtained from a local feed mill (Davis Feed Mill, Perkasie, PA). An initial series of ambient extractions, at 25°C, were carried out in a model Biostat UD, temperature- controlled 300-1 fermentor (B. Braun Biotech). A port near the bottom of the tank was fitted to allow recirculation of the maize slurry through a 20-mm tube to a model FP702 (Fristram Pump, Middletown, WI) centrifugal pump and back to the fermentor. This pump has a 6.35-mm clearance between the rotor tip and the casing. Trials with other pumps with less clearance were unsuccessful due to the jamming of the (2 mm) milled maize. The ambient extractions

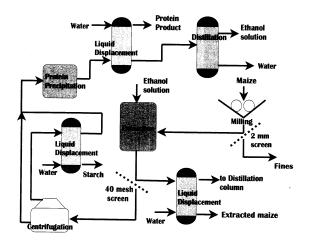


Fig. 1. Schematic diagram of maize protein extraction.

indicated that an extraction liquid composition of 70% ethanol, a liquid to solid mass ratio of 4:1, and a maize particle size of 2 mm were good ambient extraction conditions and these conditions were maintained for use at higher temperatures.

Following the extraction, the extract was drained from the maize through a 40-mesh (425um opening size) screen and pumped to a 104.8centrifuge mm tubular-bowl (Sharples, Philadelphia, PA), which rotates at 15000 rpm, generating $13200 \times g$. The fine maize particles were separated from the extract by centrifugation with a feed to the centrifuge sufficient to assure removal of 99.5% or more of the particles. Following the removal of the particles, the extract was evaporated in a vacuum evaporator at a pressure between 84 and 91 kPa at 49°C. When the liquid in the evaporator had reached the predetermined level, corresponding to a 40% ethanol concentration, the evaporator was drained and the product scraped from the bottom and walls. The scraped product was dried in a lyophilizer (2-5 days). The dry product was weighed, and the moisture, protein, lipids and starch content measured by standard wet chemical methods (AACC, 1995; AOAC, 1995; Parris et al., 1997).

2.2. Simulation

Extraction simulations were carried out using the ASPEN PLUS© package (Aspen Technology, Cambridge, MA). To carry out a simulation, a flow sheet representing the process was created and the stream rates, compositions and temperatures systematically varied to achieve a steady mass and energy balance consistent with the block and inlet stream specifications. Some unit operations were simulated with general blocks in which the parameters were set based on experimental and estimated performance. The milled maize had the following mass fractions: residual protein and starch, bran, ash, 0.265; starch, 0.654; extractable protein, 0.0569; and oil, 0.0246. Protein and oil were produced as a mixture with a mass ratio of 0.0569/0.0246. Varying fractions of the proteinoil mixture were extracted and all of the starch. The centrifuge and countercurrent displacement

Table 1
Feed, solvent, by-product and utility costs used in the simulation

Cost source	Unit cost (\$/kg)
Maize	0.13
Ethanol	0.41
Starch	0.18
Process water	0.02/t
Steam (1 MPa)	0.01
Power	0.05/kWh

equipment outputs were taken as 0.5 mass fraction liquid and the dry products as 0.11 mass fraction liquid. We determined that the cost of extracting alcohol-soluble proteins from maize can be approximated with a few parameters. The extraction process is comprised of several functional areas: (1) feed preparation; (2) extraction and solvent separation from the residual cereal; (3) spent alcohol recovery; (4) post precipitation product processing; (5) product(s) drying.

Each of these areas will have associated costs, including: (1) the cost of equipment and physical processing facility; (2) utility cost such as steam, electricity and cooling water; (3) plant labor, supplies and overhead; (4) operating materials, such as makeup ethanol and water (Tables 1-3).

Based on pilot plant and simulated extractions, we developed parameters that allow the approximation of process cost by fitting the simulation results to a simple model. The simulation and

Table 2
Estimated capital costs for an ethanol extraction facility

Item	Cost (1000\$)
Counterwash separators	1171
Centrifuges	652
Distillation tower	533
Milling equipment	111
Starch dryer	682
Zein/oil product dryer	118
Tanks	73
Heat exchangers	347
Pumps	40
Subtotal equipment	3727
Other capital costs	7454
Total capital cost	11 181

Table 3 Costs for an ethanol extraction process with an annual production of 2520 tonnes/year

Resource	Annual cost (\$1000/year)	Cost (\$/kg of product)
Corn	13 183	5.22
Steam	3405	1.36
Ethanol	888	0.35
Electricity	599	0.24
Cooling water	273	
City water	3	
Labor	609	0.24
Operating and maintenance supplies	124	0.05
General and administrative	960	0.38
Depreciation	1242	0.49
Gross operating charges	21 286	8.42
Coproduct credit	13 472	5.33
Zein/oil product cost	7814	3.09

costing program, ASPEN PLUS© release 9.3 (Aspen Technology, Cambridge, MA), was based on our specific process, the extraction of 8.2 t/h of the 2-mm fraction of milled maize, producing 309 kg/h of 95% solid zein/corn oil product. The corn separated as fines during milling and the extracted corn is fed to other corn-refining operations, such as a starch or ethanol plant. The extraction facility is assumed to operate 8160 h/year. The program did not include the cost of product or coproduct handling, packaging or storage. Sales and marketing, contingency allowances and financial charges were also excluded.

The extraction facility includes milling equipment, extraction vessels, countercurrent slurry rinse units, decanter centrifuges, dryers and a distillation unit, heat exchangers, pumps, holding tanks and a building to house the equipment. All necessary materials, labor and technical support required to operate the plant are also included. A breakdown of the capital costs and a summary of the costs for the facility costs are listed in Table 2. Equipment costs were obtained from manufacturers, the ChemcostTM Program (Chemstations, Houston, TX) a program for capital cost and profitability analysis, ASPEN PLUS© (Aspen Technology), simulation and cost program and

other in-house sources. The remaining capital costs were estimated by Lang-type cost factors (AACE, 1990; Jelen, 1970) and included costs for installation, site preparation and improvement, concrete, building and structural steel, piping, electrical equipment, instrumentation, insulation. painting, engineering and construction management and contingency allowances. The cost factors can vary over a wide range with multipliers from less than 2 to multipliers of more than 6 (Jelen, 1970), but are usually based on the characteristics of the equipment purchases. In this study, a factor of 3 was used based on the authors' experience and from replies to inquiries by engineers and constructors involved with similar projects.

Modern extraction systems are automated, but still require plant operators for monitoring, adjusting and handling plant upsets. We included two plant operators per shift for this facility. Labor cost is based on a salary of \$15.30/h plus 40% fringe benefits. The major utilities are steam, electric power and water. Because steam will be required in other processing areas in a larger facility containing an extraction unit, we used typical unit prices rather than specific generating boiler equipment. The maintenance costs are calculated at 1.7% of the plant's capital cost for labor and 1% for maintenance materials. Miscellaneous operating supplies are included at 0.5% of labor costs. General and administrative charges are 4.3% of all other production charges and property insurance charges are 0.8% of capital costs.

3. Results and discussion

The concentration of dilute solvent is a major cost element in a solvent extraction. In the simulated process, four streams of dilute solvent must be distilled to restore them to an effective extraction concentration. A fraction of the maize will not dissolve during exposure to the extraction solvent and the extract (liquid) left on this residual solid, after extraction, will be diluted when it is rinsed from the solid. Similarly, the separated starch product and protein/oil product must be

rinsed, creating dilute alcohol streams. After the extraction liquid is diluted to precipitate the product and the precipitate product removed, the liquid must be restored to its extracting concentration. Distillation is a usual way to concentrate solution streams. This cost (DstC) is a significant fraction of the overall cost and can be formulated as:

 $DstC = \alpha$ (feed to the distillation column)

where α is a factor dependent on column design, energy cost and the feed and product compositions. The distillation column feed = liquid left on solids, filtered from suspensions + rinse water + dilute extract filtered from products:

=
$$[l_1(\text{extracted maize})][1 + r_1] + [l_2(\text{starch})][1 + r_2]$$

+ $[l_3(\text{zein/oil solid})][1 + r_3]$
+ extraction liquid (d_1)

where l_i is the ratio of liquid to solid, left on the filtered solid, and r_i is the ratio of rinse water to liquid left on the solid, d_1 is the ratio of diluted to original extract solution. Because it is preferable to dilute the extract solution by evaporating ethanol under a low vacuum rather than adding water, d_1 is < 1. We also set l_i to 0.5 and r_i to 1.

Another energy-based cost is the cost of drying the products (DryC). All of the feed is converted to dry products except the extracted maize, which is pumped to the liquefaction equipment for enzymatic conversion of the unextracted starch to glucose at 50% solids. The products are to be centrifuged to 40% liquid then evaporatively dried to 11% liquid. The drying cost is then dependent on the maize fraction converted to products. DryC = β (products). As indicated in the simulation section, the product fraction used was 0.735. The cost of the centrifugal dewatering to 40% liquid is much lower than that of evaporation.

Two mass ratios are convenient variables to use to derive a formula for predicting the cost of solvent extraction: the mass ratio of soluble products recovered to feed (P/F), and the mass ratio of extraction liquid to feed (L/F). The first ratio is the protein fraction extracted multiplied by the ratio of protein fraction in the feed to the protein fraction in the product. The preceding equations can then be rewritten as:

distillation column feed = maize fed $(1 + d_1(L/F))$

$$DstC = \alpha(F)(1 + d_1(L/F))$$

$$DryC + DstC = \beta(0.735)(F) + \alpha(F)(1 + d_1(L/F))$$

where F is maize fed to process.

The net cost of the zein/oil product can be estimated by subtracting the income from byproducts and adding feed, utilities and fixed costs.

The fixed costs are divided into those pertaining to: the front end equipment, A_1 , mainly sized in proportion to F; the extraction and immediate downstream equipment, A_2 , sized in proportion to L; and the post-product precipitation equipment, A_3 , sized in proportion to P.

Thus specific product cost (\$/kg)

=
$$[A_1(F) + A_2(L) + A_3(P) + \text{DstC} + \text{DryC} + \text{maize cost} - \text{by-products value}]/P$$
.

We set the cost of extracted maize and of the starch product per unit mass equal to that of maize (m),

Product cost =
$$[A_1(F) + A_2(L) + A_3(P) + \alpha(F(1 + d_1(L/F))) + \beta(0.735)(F)$$

 $- P(m)]/P$
= $[A_1 + A_2(L/F) + A_3(P/F) + \alpha(1 + d_1(L/F)) + \beta(0.735)$
 $- m(P/F)]/(P/F)$
= $(c_1 + c_2/(P/F) + c_3(L/F)/(P/F))$ (1)

where

$$c_1 = A_3 - m$$

 $c_2 = \alpha + \beta (0.735) + A_1$
 $c_3 = A_2 + \alpha d_1$.

Examination of reasonable values for the coefficients c_i , which were derived from cost estimates generated by simulation of an extraction feed, F, of 200 tonne was used to determine some of the underlying coefficients. Plots of cost versus L/S for constant values of P/F were made and the slopes then fit to a linear function of P/F. The fits were made using a numerical package (RS/1,

BBN Software Products, Cambridge MA). A series of runs with 0.039 < P/F < 0.0645 and 2 < L/F < 2.5, which are reasonable targets, yielded

 $c_1 = 0.13 \pm 0.02 \, \text{\$/kg}$

 $c_2 = 0.075 \pm 0.002 \, \text{\$/kg}$

 $c_3 = 0.010 \pm 0.0004 \, \text{\$/kg}$

with m = 0.13 (\$/kg), $A_3 = 0.26$ (\$/kg). From the variable costs, $\alpha = 0.004$ and, to the accuracy of other estimated values, $\alpha = \beta$; consequently $A_1 = 0.0027$. A_2 can be determined using $d_1 = 0.3$, to be 0.0032. As expected, the relative size of the terms in Eq. (1) suggests that, in this case, the product cost is mostly ($\sim 75\%$) determined by the cost of the energy needed to distill the solvent. The most expensive fixed cost components are those related to the separation of fine solids at the product end of the process. Fine solid separation equipment will also be the most difficult to design.

Chen and Hoff (1987) reported extracting milled maize with 95% ethanol, and then extracting it with a 50% ethanol solution in a packed column. This process used a L/F ratio of 0.75, 6 h and achieved a 40% recovery of the zein (P/F)= 0.04) in the form of a 2.8% (w/v) solution. By comparing this process with the one used to develop the correlation, the most obvious differences are the low L/F ratio and the longer extraction time. The Chen process requires approximately six times greater capital cost (A_2) per unit liquid flow, but the flow rate will be only (0.75/2.5) = 0.3 as great. As indicated for the 'standard' process, solvent reconcentration is the major cost generator. With a flow of only 0.3 that of our standard and an ethanol concentration change of only 50-40% ethanol, the Chen process would be cheaper. However, extraction of oil with 95% ethanol would be more expensive because this ethanol would have to be reconcentrated from the dilute solution separated by displacement or evaporated from the corn.

The correlation can be used to estimate the cost of extraction of protein from cereal grains. With the increased capability to deliberately alter cereal genomes, it seems likely that seed with increased protein would become available in the near future. Our estimates provide an initial means of

deciding whether such a variant would be worth developing; assuming other seed qualities were not impaired (yield, resistance to disease and pests, etc.). Increasing protein content (P/F) will reduce extraction cost. L/S = 3 is close to the minimum value of this ratio, and independent of protein content. Product yield will rise with P/F, limited only by solubility. Maize extractions reusing extract solution with L/S = 3 demonstrated that protein can be extracted using a liquid with protein concentration of at least three times the concentration of a single extraction extract. Thus, for P/F up to at least 0.1, the estimated cost from Eq. (1) becomes (0.13 + 0.10)(P/F)) \$/kg. As part of initial feasibility studies of protein extraction from grains other than maize, investors can use this correlation and the appropriate estimates of the protein yield (P/F), and solvent required (L/F), to estimate extraction cost.

4. Notation

 A_1 fixed costs proportional to feed (\$/kg)

 A_2 fixed costs proportional to extracting liquid flow rate (\$/kg)

 A_3 fixed costs proportional to sum of product streams (\$/kg)

 c_i coefficients in reduced equation of specific product cost (\$/kg)

DstC distillation cost (\$)

DryC product drying cost (\$)

d₁ mass ratio of diluted solvent to extract solution

F maize flow (kg)

P product flow (kg)

L extracting solvent flow (kg)

mass ratio of liquid to solid on

product i

m cost of maize (\$)

 r_i mass ratio of rinse to residual solvent on rinsed product i

4.1. Greek letters

 α distillation cost (\$/kg) β drying cost (\$/kg)

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